Report and implications of the first observation of C_4N_2 in laboratory simulations of Titan's atmosphere

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Abstract

C_4N_2 is an exceptional organic compound in Titan; it is the only one to have been detected in condensed phase but not in gas phase. After the description of the delicate C_4N_2 laboratory synthesis and of the determination of C_4N_2 mass spectrum, we report here the first identification of gaseous C_4N_2 in laboratory simulations of Titan's atmosphere, using our last experimental system, based on a N_2–CH_4 cold plasma at low temperature and low pressure. Finally, we discuss the implications of this identification in the frame of remote sensing observations of gaseous C_4N_2 in Titan's atmosphere. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The Voyager spacecrafts were not able to penetrate the thick layers of clouds but they did reveal that Titan is one of the most interesting places in the solar system. The Voyager infrared spectrometer (IRIS) was able to detect many organic compounds (hydrocarbons and nitriles). Maguire et al. (1981) and Sagan and Thompson (1984) demonstrated that the abundance of many compounds detected by IRIS allow their condensation in Titan's atmosphere. Later some condensed species were identified. In 1987, an unblended emission feature at 478 cm^{-1} in some spectra of Titan's north polar cap was identified as the ν_8 band of solid C_4N_2 (Khanna et al., 1987). But the corresponding gas phase band at 471 cm^{-1} was undetected.

C_4N_2 is an exception in Titan's detected organic compounds; it is the only one to have been detected in condensed phase but not in gas phase. Many experiments have been carried out in the laboratory to simulate the chemical evolution and the synthesis of organic compounds in Titan's atmosphere, under the action of different energy sources (Gupta et al., 1981; Toupance et al., 1975; Raulin et al., 1982; Thompson et al., 1991; de Vanssay et al., 1995; Coll et al., 1995). UV flux, energetic particles, electrons or plasmas could induce chemical evolution in a N_2–CH_4 mixture (main constituents of Titan's atmosphere). When looking at the list of organic compounds which have been identified in those experiments, one can notice a quite satisfactory agreement with observations (Table 1). In fact, only one compound except for oxygenated compounds (not resulting from a N_2–CH_4 mixture chemistry) has been detected in Titan's atmosphere and not under such simulation condition — C_4N_2.

Our first attempt to detect C_4N_2 in such experimental simulation was unsuccessful (Coll et al., 1995). We detected some organic compounds unstable at room temperature, especially C_6H_2 and HC_5N. The first detection of such compounds in experimental simulation of Titan's atmosphere confirms the presence of

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Table 1
Non-oxygenated compounds detected in experimental simulation (M, major products; <, less abundant by one order of magnitude; ≪ by two orders or more)

Compounds	Titan	UV[a]	Arc and silent discharge[a]	Low temp. arc[a]
N_2 (%)	90–98	90	90	90
CH_4 (%)	2–5	10	10	10
C_2H_6	M	M	<	<
C_2H_4	≪	≪	<	<
C_2H_2	<		M	<
C_3H_8	<	≪	≪	≪
CH_3C_2H	≪		<	<
C_4H_2	≪		≪	≪
HCN	<		M	M
C_2N_2	≪		≪	≪
CH_3CN	≪		<	<
HC_3N	≪		<	<
C_4N_2	Solid			

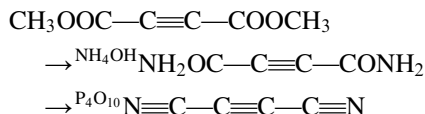[a] References in Thompson et al. (1991), de Vanssay et al. (1995), Coll et al. (1995; 1999).

polyynes and cyanopolyynes in the chemical scheme of Titan's atmosphere (de Vanssay et al., 1995; Coll et al., 1995).

The purpose of this work is to detect C_4N_2 in a simulation of Titan's atmosphere. In a first part we will describe the delicate synthesis protocol, especially developed for this study. Then we will present the work of characterization of produced C_4N_2 (mass spectrum), with its problem of instability. We will finally describe Titan's atmosphere simulation, including of course C_4N_2 detection, and we will conclude with the implications of such identification.

2. C_4N_2 synthesis

Dicyanoacetylene was prepared by a method derived from that described by Moureu and Bongrand (1909), using the reaction starting from 2-butynedioic acid dimethyl ester:

$$CH_3OOC\!-\!C\!\equiv\!C\!-\!COOCH_3$$
$$\xrightarrow{NH_4OH} NH_2OC\!-\!C\!\equiv\!C\!-\!CONH_2$$
$$\xrightarrow{P_4O_{10}} N\!\equiv\!C\!-\!C\!\equiv\!C\!-\!C\!\equiv\!N$$

Dimethyl acetylene dicarboxylate (2-butynedioic acid dimethyl ester) was purchased from Aldrich.

First, 100 ml of aqueous ammonia (28%) are introduced into a 250 ml two-necked round-bottomed flask, equipped with an efficient magnetic stirrer and a nitrogen inlet. The flask is immersed in a bath cooled to −40°C. When the temperature of the aqueous ammonia rises to about −35°C and just before crystallization, the 2-butynedioic acid dimethyl ester (7.1 g, 50 mmol) is slowly added. The solution is allowed to warm to room temperature in about 30 min and the excess ammonia is then removed in vacuo. The crude 2-butynediamide (5.1 g, 90% yield) is obtained as crystals and used in the following step without further purification.

A vacuum line is equipped with a stopcock and cold finger. Into a 100 ml one-necked round bottomed flask equipped with a magnetic stirrer are introduced dry and finely divided 2-butynediamide crystals (3.3 g), dry sea sand (30 g) and P_2O_5 in excess (14 g). The mixture is cautiously stirred; the flask is fitted onto the vacuum line, stirred further and then degassed. The trap is immersed in a cold bath at −80°C. The flask is slowly heated to 230°C using an oil bath; the dicyanoacetylene condenses in the cold trap and the products with low boiling points are evacuated in the pump. At the end of the reaction, the flask is disconnected from the vacuum line, the cold finger is filled with liquid nitrogen and the trap is allowed to warm up to room temperature. Pure dicyanoacetylene condenses on the finger. The product (0.6 g, 25% yield) is then transferred in vacuo to a Schlenk flask.

Table 2
Mass spectrometer analysis conditions

|	Titan's simulation experiment	C_4N standard analysis
Multiplier set voltage	1550 V	1600 V
Manifold set temperature	200°C	200°C
Emission set current	10 μA	10 μA
A/M amplitude set voltage	2.5 V	2.5 V
Low mass	12 amu	15 amu
High mass	650 amu	100 amu
Scan rate	1500 ms	1000 ms
Threshold	0 counts	0 counts
Filament delay	1 s	1 s
Mass defect	100 millimass/100 amu	100 millimass/100 amu
Background mass	12 amu	12 amu
Scan mode	Electronic ionization	Electronic ionization
Ionization control	Automatic	Automatic
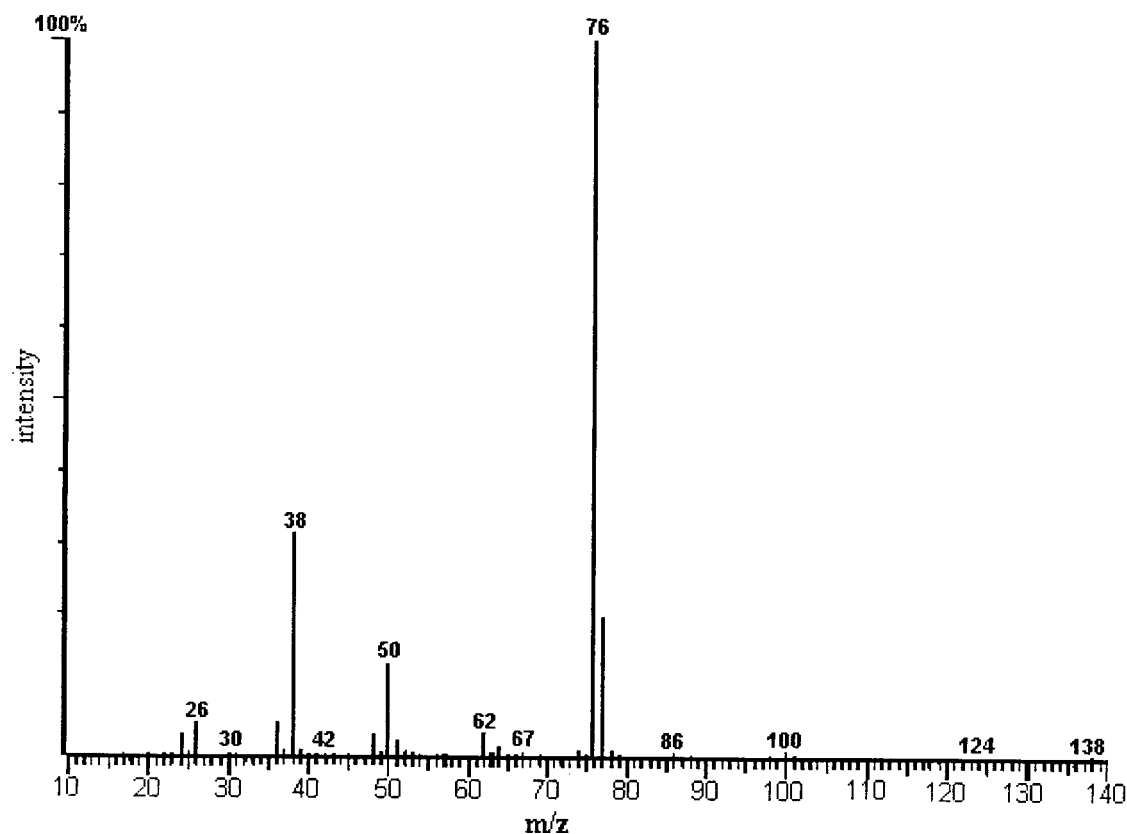
Fig. 1. Standard C_4N_2 mass spectrum ($m/z = 26$ corresponds to $[C\equiv N]^+$, $m/z = 38$ to $[C-C-N]^+$ and $m/z = 50$ to $[C\equiv C-C\equiv N]^+$ fragments).

3. C_4N_2 standard mass spectrum

A set of injections of synthesized C_4N_2 at very low concentration in the GC-MS, using the experimental conditions described above in Table 2, always gives a GC peak at 4 min 50 s. Then we recorded the mass spectrum of this compound, that appears quite similar to the 2-butynenitrile (C_4N_2) reference in the NIST library (de Vanssay et al., 1995). This spectrum is shown in Fig. 1.

The main signal is the molecular peak $m/z = 76$, and the mass ($m + 1$) is always present. Three other fragments are also present, $m/z = 26$, $m/z = 38$ and $m/z = 50$, respectively corresponding to the $[C\equiv N]^+$, $[C-C\equiv N]^+$ and $[C\equiv C-C\equiv N]^+$ fragments.

4. C_4N_2 detection limit

Three years ago, our first attempt to detect C_4N_2 in the gas phase of a Titan's atmosphere laboratory simulation was unsuccessful (Coll et al., 1995).

To understand the reason of this failure, the GC and MS behavior of C_4N_2 have been studied in more detail (Aflalaye et al., 1995). As an example its stability

was quantitatively studied. We have diluted (1/1000) C_4N_2 in N_2, and kept the diluted sample at room temperature for various durations, t, and analyzed it by GC-MS. The relative quantity of C_4N_2 remaining in the sample as a function of time is presented in Fig. 2. After an only slight observed decrease during the first 15 min, the relative concentration of C_4N_2 strongly decreases and reaches about 0 in less than 1 h, with a
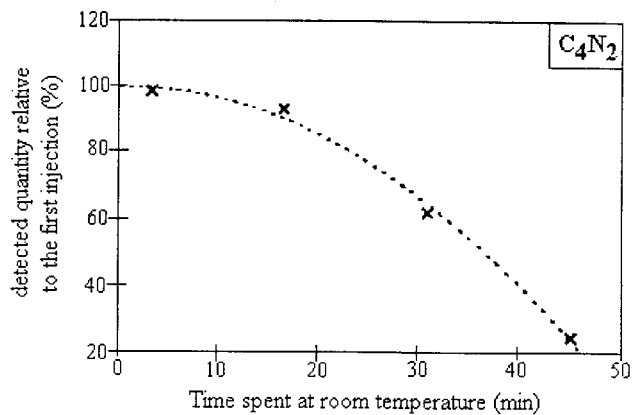

Fig. 2. Relative quantity of gaseous C_4N_2 remaining in a sample as a function of time.
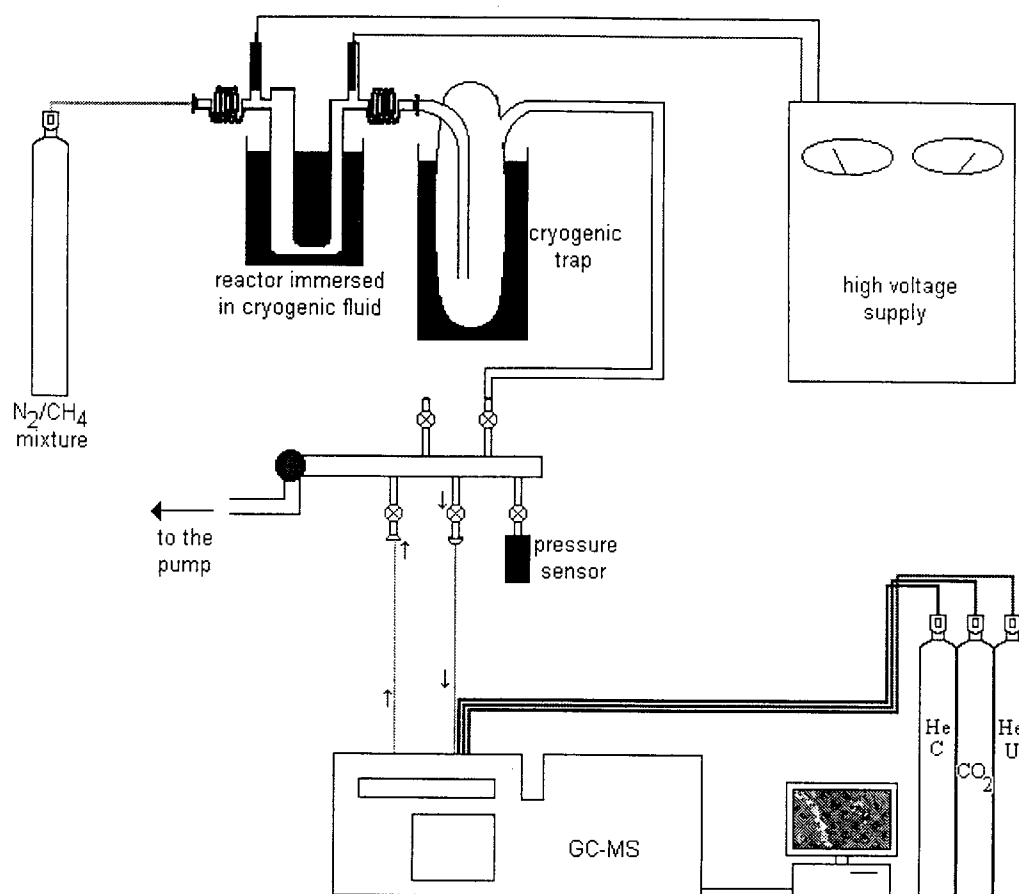
Fig. 3. Experiment devoted to qualitative and quantitative studies of gaseous compounds produced during the laboratory simulations of Titan's atmosphere (analysis by gas phase chromatograph coupled with mass spectrometry).

lifetime of about 35 min. Such results can be interpreted as a complex polymeric reaction with slow initiation processes, and fast secondary steps due to an autocatalytic process.

In a second step, we tried to determine the detection limit of C_4N_2 in the experimental MS conditions described in Table 2. Using the highest MS sensitivity (the MS detector being tuned on specific mass $m/z = 76$), C_4N_2 is detected when 500 pg are injected into the GC column, which was not the case when injecting only 423 pg (Coll et al., 1995). It is important to note that other nitriles, within the same conditions, present a detection limit of about 10 pg or even less. Thus, the non-detection of C_4N_2 (in case of formation) during these experiments, is not only due to the low stability of this compound, but also to the low sensitivity of the GC-MS analytical techniques towards this dinitrile.

5. Titan's atmosphere experimental simulation

The reactor developed for this program is a U-tube

(Fig. 3), approximately 25 cm high, with an internal diameter of 1.8 cm for the left part and of 0.9 cm for the right part. Iron electrodes are inserted into each end of the tube. They are protected with a mica film to avoid metallization of the reactor. A low pressure flux (total pressure: ≈ 2 mbar) of a mixture of N_2–CH_4 (98:2) passes through the reactor, and a high voltage (≈ 4000 V, direct current, with a circuit internal resistance of 22 kΩ) is established between the electrodes. The current raises to ≈ 80 mA, and a glow discharge (or cold plasma) is then established inside the reactor. The reactor can be immersed in a cryogenic fluid. A cold trap can be added between the output of the reactor and the pumping unit to collect outgoing gases by condensation (Fig. 3). To collect tholins samples (Coll et al, 1999), the reactor is put inside a glove box which is filled with nitrogen, then samples are obtained without contamination. The top of the reactor can be opened for introduction of collector plates or for sampling the aerosol analogues.

The cold plasma reactor described above is submitted to eight-hour irradiations. During this time, a volume of N_2–CH_4 mixture corresponding to 1.78
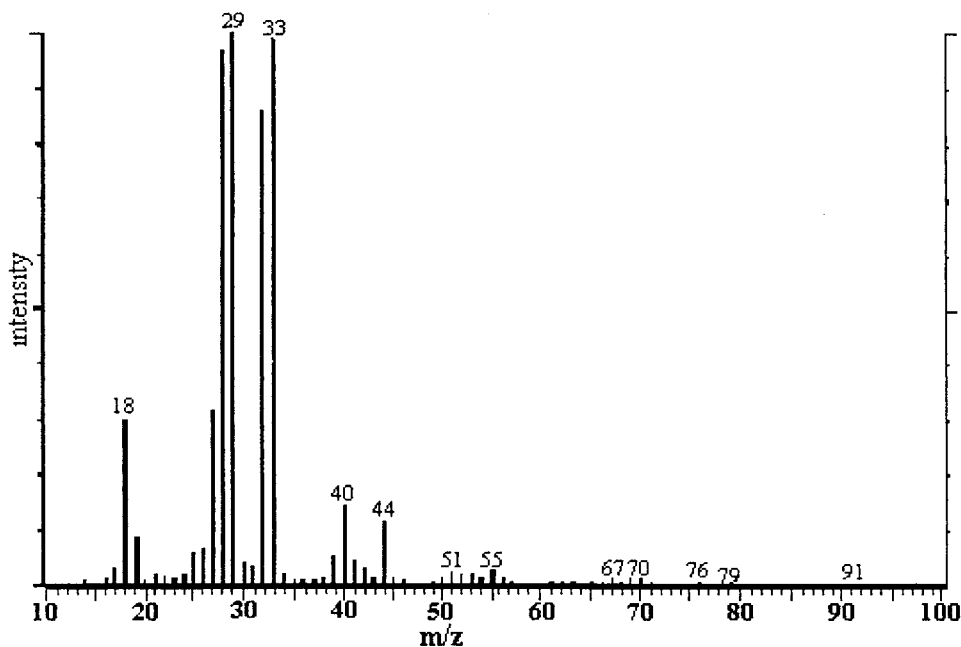
Fig. 4. Total mass spectrum at 8 min 15 s (simulated gas phase elution).

moles of gas, moves through the reactor. The temperature of the simulation system was reproducible but could not be directly measured. However, we have determined that it was in the range of 100–150 K and was maintained constant during each experiment. The deposited energy was determined using an actinometry
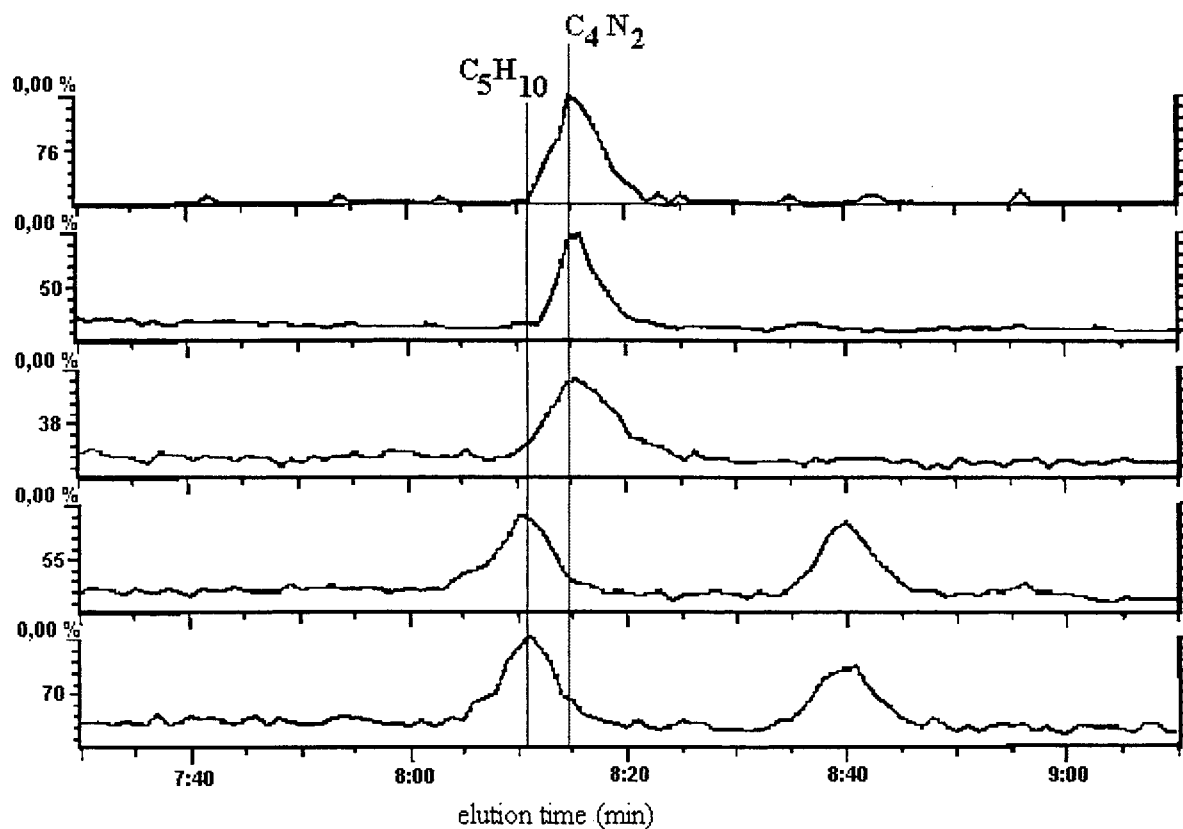

Fig. 5. Mass by mass spectra between 7 min 30 s and 9 min 10 s (mass 76, 50, 38, 55 and 70).
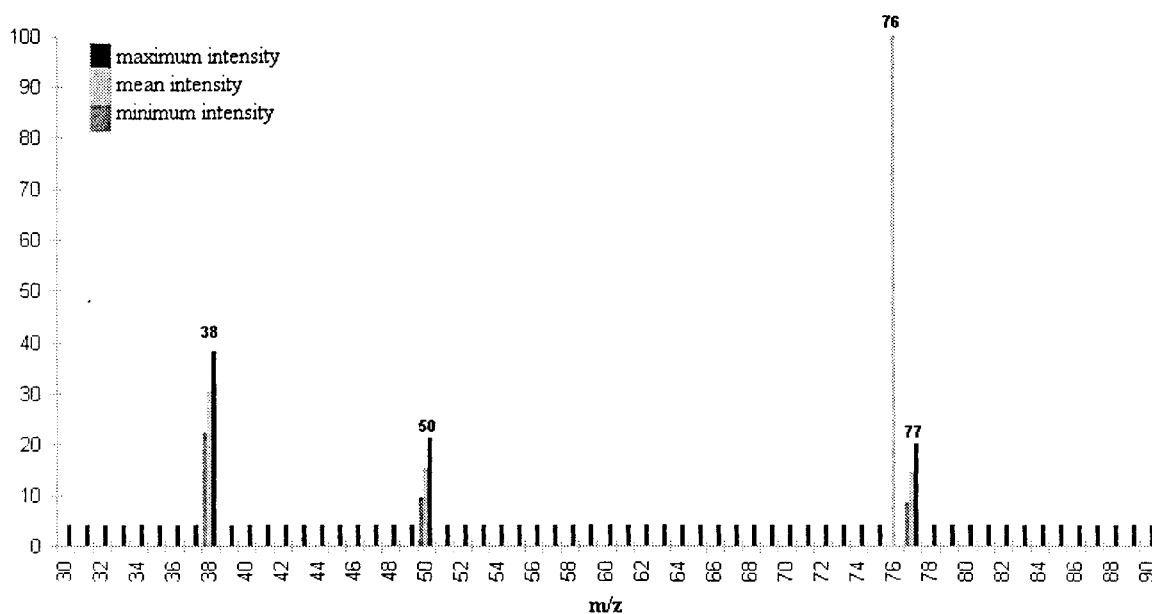
Fig. 6. Computed mass spectrum of detected C_4N_2 from simulation experiment.

method based on C_2H_4 irradiation, which gives rise to C_2H_2, H_2 and CH_4. There is a known correlation between the C_2H_2 yield (molecules/100 eV) and the pressure of C_2H_4 (Sauer and Dorfman, 1961). In this way we were able to estimate the energy deposited to the reactant gas mixture, at 1.5 mbar, to be 9×10^{24} eV, corresponding to a maximum of 8.4 eV molecule^{-1}.

The mixture of gases formed during experimental simulation was analyzed: 44 hydrocarbons and 26 N-containing compounds were identified by GC-MS during a run. For a more complete description of the protocol and of the results, see Coll et al. (1999).

6. C_4N_2 detection in such simulation

During the analysis of the gas phase resulting from a simulation of Titan's atmosphere, we tried specifically to find all the $m/z = 76$ signals (that we will refer to as 'peak 76'), because this is the main fragment of the C_4N_2 mass spectrum. That research was led in a delimited area of the chromatogram, known as the C_4N_2 standard retention time in such GC conditions. The elution of C_4N_2 was expected to take place between those of but-3-en-1-yne and propanenitrile.

All the observed peaks 76 were part of the mass spectrum of identified products, except one, located at the elution time of 8 min 15 s. The global mass spectrum related to this elution time is reported in Fig. 4. There are two views on the matter:

1. this 76 peak is a minor signal from the mass spectrum, which main principal peaks are 40, 44, 55, 70

   ...

2. the global mass spectrum is the result of several product coelutions.

Considering the possibility of a coelution, we decided to conduct a study of the specific mass chromatograms, in order to observe the evolution in time of the various signals. This experiment led us to clearly establish that the global signal did result from a coelution, the first product (peak 55, peak 70 ...) having an elution time of 8 min 11 s and the second one eluting at 8 min 15 s (see Fig. 5).

The two signals could further be separated, by studying for each mass the detected signal intensity as a function of time. The main difficulty of this step was the fact that the signal of the second product remained hidden by the end of the first compound elution signal. After comparison with compounds from the NIST library, the first product was identified as a C_5H_{10} isomer. The computed mass spectrum of the second product is presented in Fig. 6, where the maximum, minimum and mean intensity of each signal are reported, on a scale normed to the intensity of peak 76. The comparison of this spectrum with that of Fig. 1 clearly confirms the identification of this hidden product as C_4N_2, which is therefore detected for the first time in laboratory simulations of the Titanian atmosphere.

7. Implications of such discovery

First of all, the identification of C_4N_2 in such experiments gives weight to the discovery of condensed

C_4N_2 in Titan's atmosphere, which was only based on its v_8 band. The existence of chemical ways for the formation of gaseous C_4N_2 in Titan's atmosphere is put in evidence by our experiment. Thus, investigations of associated photochemical mechanisms are of increased interest (Yung, 1987). In this work, it is proposed that C_4N_2 formation is due to the presence of nitrogen atoms in the high atmosphere, which are responsible for the following mechanism

$$C_2H_2 + N(^2D) \rightarrow CHCN + H \text{ then } 2\, CHCN \rightarrow C_4N_2 + H_2$$
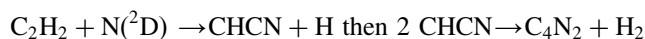
The next challenging step is the effective identification of gaseous C_4N_2 in Titan's atmosphere. So as reach this objective, the gas infrared spectra, assignments and absolute IR band intensities of C_4N_2 in the 250–3500 cm^{-1} region have been determined at LISA (Khlifi et al., 1997), as well as the temperature dependence of gaseous C_4N_2 mid-UV absorption coefficients (Bénilan et al., 1996). Is it therefore possible to detect C_4N_2 gas phase on Titan?

Khlifi et al. (1997) have especially studied C_4N_2 bands in the 1200–200 cm^{-1} range, and have derived from IRIS observations in this range an upper limit for the C_4N_2 abundance. They have predicted an upper limit of 8.5 ppb in Titan's stratosphere. Using a radiative transfer program, Samuelson et al. (1997) have determined an upper limit of 4×10^{-10} for the C_4N_2 vapor mole fraction, and a corresponding upper limit of 90 km for the cloud top. But they have also demonstrated that the condensate phase is not in equilibrium with the gaseous phase (the condensate phase is 50 to 200 times more abundant), and explained that this non-equilibrium state is due to a cyclic dependent process. In fact, the authors hypothesis is that at the season of Voyager 1 polar measurements, gaseous C_4N_2 was being destroyed in the upper atmosphere by photochemistry since the end of winter, while condensed C_4N_2 remained at lower altitude, before its destruction throughout the season. This phenomenon could explain the surprising 50:200 ratio between the 2 phases, as well as the detection by IRIS of only the condensate phase.

Voyager 2 arrived around Titan on next winter, but not on a trajectory that allowed the study of the north pole. The problem was the same with ISO, which measurements were mainly obtained on the equator, region that seems to be too much exposed to sunlight to avoid C_4N_2 formation.

The best chance to obtain a identification of gaseous C_4N_2 on Titan's atmosphere, before Cassini–Huygens mission results, may come from the *Hubble Space Telescope* observations in the UV, taking benefit of laboratory determinations of Bénilan et al. (1996). In this case, HST needs to point to north polar region,

during the winter season, in order to maximize the probability of detection.

8. Conclusion

After developing a specific synthesis for C_4N_2 production, we have established its mass spectrum. C_4N_2 traces also need a specific data treatment to be detected in a forest of peaks. Finally this detection confirms that formation of gaseous C_4N_2 in Titan's environment could occur, probably by the way of the following reaction:

$$C_2H_2 + N(^2D) \rightarrow CHCN + H \text{ then } 2\, CHCN \rightarrow C_4N_2 + H_2$$

The next step will be the vapor phase detection of C_4N_2 in Titan's atmosphere. The best location for such observations seems to be the north polar part of the atmosphere, where the C_4N_2 sink (i.e. photochemistry) is limited in winter. Waiting for Cassini–Huygens measurements in 2004, the best chance to reach such detection seems to be a taking aim of HST on the north pole.

References

Aflalaye, A., Andrieux, D., Bénilan, Y., Bruston, P., Coll, P., Coscia, D., Gazeau, M.C., Khlifi, M., Paillous, P., Sternberg, R., de Vanssay, E., Guillemin, J.C., Raulin, F., 1995. Thermally unstable polyynes and N-organics of planetological interest: new laboratory data and implications for their detection by in situ and remote sensing techniques. Adv. Space Res. 15 (10), 5–11.

Bénilan, Y., Andrieux, D., Khlifi, M., Bruston, P., Raulin, F., Guillemin, J-C., Cossart-Magos, C., 1996. Temperature dependence of HC_3N, C_6H_2, and C_4N_2 mid-UV absorption coefficients: application to the interpretation of Titan's atmosphere spectra. Astrophysics and Space Science 236, 85–95.

Coll, P., Coscia, D., Gazeau, M.C., de Vanssay, E., Guillemin, J.C., Raulin, F., 1995. Organic chemistry in Titan's atmosphere: new data from laboratory simulations at low temperature. Adv. Space Res. 16 (2), 93–103.

Coll, P., Coscia, D., Smith, N., Gazeau, M-C., Ramirez, S.I., Cernogora, G., Israël, G., Raulin, F., 1999. Experimental laboratory simulation of Titan's atmosphere (aerosols and gas phase), Planet Space Science, in press.

Gupta, S., Ochiai, E., Ponnamperuma, C., 1981. Organic synthesis in the atmosphere of Titan. Nature 293, 725–727.

Khanna, R.K., Perera-Jarmer, M.A., Ospina, M.J., 1987. Vibration infrared and Raman spectra of dicyanoacetylene. Spectrochim. Acta 43A, 421–425.

Khlifi, M., Paillous, P., Bruston, P., Guillemin, J-C., Bénilan, Y.,

Daoudi, A., Raulin, F., 1997. Gas infrared spectra, assignments, and absolute IR band intensities of C_4N_2 in the 250–3500 cm^{-1} region: implications for Titan's stratosphere. Spectrochimica Acta Part A 53, 707–712.

Maguire, W.C., Hanel, R.A., Jennings, D.E., Kunde, V.G., Samuelson, R.E., 1981. C_3H_8 and C_3H_4 in Titan's atmosphere. Nature 292, 683–686.

Moureu, C., Bongrand, J.E., 1909. Bull. Soc. Chim. V, 846.

Raulin, F., Mourey, D., Toupance, G., 1982. Organic syntheses from CH_4–N_2 atmospheres: implications for Titan. Origins of Life 12, 267–279.

Sagan, C., Thompson, W.R., 1984. Production and condensation of organic gases in the atmosphere of Titan. Icarus 59, 133–161.

Samuelson, R.E., Mayo, L.A., Knuckles, M.A., Khanna, R.J., 1997. C_4N_2 ice in Titan's north polar stratosphere. Planet. Space Sci. 45, 941–948.

Sauer, M.C., Dorfman, L.M., 1961. The radiolysis of ethylene: details of the formation of decomposition products. J. Phys. Chem. 66, 322–325.

Thompson, W.R., Henry, T.J., Schwartz, J.M., Khare, B.N., Sagan, C., 1991. Plasma discharge in $N_2 + CH_4$ at low pressures: experimental results and applications to Titan. Icarus 90, 57–73.

Toupance, G., Raulin, F., Buvet, R., 1975. Formation of pre-biochemical compounds in models of the primitive Earth's atmosphere: CH_4–NH_3 and CH_4–N_2 atmospheres. Origins of Life 6, 83.

de Vanssay, E., Gazeau, M.C., Guillemin, J.C., Raulin, F., 1995. Experimental simulation of Titan's organic chemistry at low temperature. Planet. Space Sci. 43, 25.

Yung, Y.L., 1987. An update of nitrile photochemistry on Titan. Icarus 72, 468–472.